DOI: 10.15826/chimtech.2016.3.1.003

V. Tkach[1,2], C. S. de Oliveira [2], J. Maia [2], Soares B. Gunter [3], R. Ojani [4], P. I. Yagodinez[1]

[1] Chernovitsky national University, Ukraine
[2] Federal University of state of Mato Grosso do Sul, Brazil
[3] Federalny the state University of Rio de Janeiro, Brazil
[4] University of Mazandaran, Islamic Republic of Iran
E-mail: nightwatcher2401@gmail.com

The mathematical description of the electrosynthesis of composites of oxy-hydroxycompounds cobalt with polypyrrole overooxidazed

The electrosynthesis of the composite with of the overoxidized polypyrrole with cobalt oxy-hydroxide in strongly acidic media has been described mathematically, using linear stability theory and bifurcation analysis. The steady-states stability conditions and oscillatory and monotonic instability requirements have been described too. The system´s behavior was compared with behavior of other systems with overoxidation, electropolymerization of heterocyclic compounds and electrosynthesis of the cobalt oxy-hydroxides.

Keywords: cobalt, polypyrrole, overoxidation, oscillations, stable steady-state.

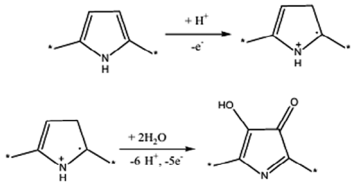
Introduction

Electrically conducting or conducting polymers (CP) occupy their place among the most studied materials during the last 50 years [1–4], due to their ability to combine the properties of plastics (flexibility and corrosion resistance) with metallic conductivity, so they are called synthetic metals. Another advantage that they possess is the ease of modification, giving them a wide and rich range of applications, from anticorrosive coatings to sensors and biosensors [5–12].

On the other hand cobalt is one of the most commonly used metals [13-14]. Its oxy-hydroxycompounds, in the form of films, can be used as anticorrosion coatings, as well as the surfaces for photoelectrocatalysis, due to to their intensively black color [15–16], therefore, their composites with conducting polymers should also exhibit interesting properties.

However, the oxidation of compounds of bivalent cobalt to trivalent occurs at relatively high potentials (from +1.6 V),

in which some conducting polymers, such as polypyrrole [17–18], undergo a process



(1–2)

of so-called "overoxidation", known as reconfiguration of the conjugated system in the polymer according to the following mechanism.

Thus overoxidative polypyrrole conducts electricity worse than neutral. Another problem may be caused by electrochemical oscillatory and monotonic instabilities, capable to accompany the processes of electrochemical oxidation of small organic molecules (including electropolymerization [19–28]), and conducting polymers [29–32]. The oscillations also accompany the process of CoO(OH) formation [15–16]. The study of their causes is one of the key stages to determine the most probable mechanism of this process.

So far, such phenomena has gained only phenomenological interpretation, which, though it may proceed from a logical conviction, has no solid theoretical justification, that can be given only by analyzing mathematical models, can adequately describe the process, which will be done in this work.

This analysis can explain the behavior of such systems and (as a consequence of the theorem of Kirpichev and Guchman) compare them with other similar systems are described, for example in [33–49].

System and model

For the mathematical description of potentiostatic electrosynthesis of the composite of the overoxidized polypyrrole with CoO(OH), from neutral polypyrrole in strongly acidic media without fluorine ions, we introduce three variables: c – concentration of ions of bivalent cobalt in the surface layer; θ – degree of surface filling overoxidized polypyrrole; h is the concentration of protons in the surface layer.

To simplify the model, we suppose that the reactor is intensively stirring, and the supporting electrolyte is in excess, allowing neglect the influence of convective and migration flows. The thickness of the surface layer, the concentration profile of cobalt salts and protons, assumed to be linear, is constant and equal to δ.

The protons diffuse in surface layer by their diffusion and are formed as a result of the process of overoxidation, their concentration in the surface layer decreases due to proton attack of overoxidative polypyrrole. Thus, considering the first law and Fick coefficient modeling related to electric double layer (EDL), the balance equation of the concentration of protons will look like:

$$\frac{dh}{dt} = \frac{2}{\delta}\left(\frac{D}{\delta}(h_0 - h) + r_o - r_a\right), \qquad (1)$$

where h_0 is the concentration of protons in the bulk solution, r_o is the speed of the process of overoxidation, r_a is the rate of proton attack of overoxidative polymer.

The conventional conductive polymer, occupying in the beginning of the reaction the entire electrode, overoxidizes. Thus, overoxidated polymer interacts with the cobalt salt, forming a composite with the product of its oxidation, and is attacked by protons. Thus, the balance equation for the concentration of the overoxidative polymer can be written as

$$\frac{d\theta}{dt} = \frac{1}{\Gamma}(r_o - r_a - r_c). \qquad (2)$$

In which r_c is the reaction rate of the composite formation, and Γ is the polymer maximum surface concentration.

The cobalt salt diffuses to the anode, and then oxidized in the overoxidative polypyrrole with the formation of the composite and the overoxidation product. Thus, the balance equation of its concentration in the subsurface layer can be written as:

$$\frac{dc}{dc} = \frac{2}{\delta}\left(\frac{\Delta}{\delta}(c_0 - c) - r_c\right), \qquad (3)$$

being C_0 is the concentration of the cobalt salt in the solution bulk. The rate of the correspondent reactions can be expressed as:

$$r_o = k_o(1-\theta)h\exp\left(\frac{n_1 F\varphi_0}{RT}\right) \quad r_a = k_a\theta_h.$$

$$r_c = k_c\theta_c \exp\left(\frac{n_2 F\varphi_0}{RT}\right), \qquad (4\text{–}6)$$

where the k parameters represent rate constants of respective reactions, parameters n is the number of electrons transferred in electrochemical processes, φ_0 is the potential drop of the EDL, in comparison with the potential of zero charge $F = N_A \cdot e$ is the number of Faraday.

Differential equations (1–3) resemble the systems of equations, described for the case of polypyrrole overoxidation in a strongly acidic media [33], and for the case of the electrosynthesis of oxyhydroxycompounds of cobalt [34], so it is possible to confirm the third theorem of similarity. However, in order to prove the behavior of such systems, it is necessary to compare the investigation of the mentioned systems with the system of equations (1–3), as will be illustrated below.

Results and discussion

In order to research the behavior of the system with potentiostatic electrosynthesis of composite of CoO(OH) – the overoxidative polypyrrole in strongly acidic media, it is necessary to investigate the system of differential equations (1–3), taking in account the algebraic relations (4–6), using linear stability theory. Functional Jacobi matrix, the elements of which are computed for a stationary state is represented in the form:

$$\begin{pmatrix} a_{1_1} & a_{1_2} & a_{1_3} \\ a_{2_1} & a_{2_2} & a_{2_3} \\ a_{3_1} & a_{3_2} & a_{3_3} \end{pmatrix}, \qquad (7)$$

where:

$$a_{1_1} = \frac{2}{\delta}\left(-\frac{D}{\delta} + k_o(1-\theta)\exp\left(\frac{n_1 F\varphi_0}{RT}\right) - k_a\theta\right).$$

$$a_{1_2} = \frac{2}{\delta}\left(k_o h\exp\left(\frac{n_1 F\varphi_0}{RT}\right) + k_o h\theta\alpha\exp\left(\frac{n_1 F\varphi_0}{RT}\right) - k_a h\right).$$

$$a_{1_3} = 0.$$

$$a_{2_1} = \frac{1}{\Gamma}\left(k_o(1-\theta)\exp\left(\frac{n_1 F\varphi_0}{RT}\right) - k_a\theta\right).$$

$$a_{2_2} = \frac{1}{\Gamma}\left(k_o h\exp\left(\frac{n_1 F\varphi_0}{RT}\right) + k_o h\theta\alpha\exp\left(\frac{n_1 F\varphi_0}{RT}\right) - k_a h - k_c c\exp\left(\frac{n_2 F\varphi_0}{RT}\right) - k_c\alpha\theta c\exp\left(\frac{n_2 F\varphi_0}{RT}\right)\right).$$

$$a_{2_3} = \frac{1}{\Gamma}\left(-k_c\theta\exp\left(\frac{n_2 F\varphi_0}{RT}\right)\right)$$

$$a_{3_1} = 0.$$

$$a_{3_2} = \frac{2}{\delta}\left(-k_c c \exp\left(\frac{n_2 F\varphi_0}{RT}\right) - k_c \alpha\theta c \exp\left(\frac{n_2 F\varphi_0}{RT}\right)\right)$$

$$a_{3_3} = \frac{2}{\delta}\left(-k_c \theta \exp\left(\frac{n_2 F\varphi_0}{RT}\right) - \frac{\Delta}{\delta}\right). \quad (8–15)$$

The Oscillatory instability in this system is possible, because the necessary conditions of Hopf bifurcation may be satisfied. They are performed in the case of the main diagonal of the Jacobian positive elements: In this system there are three positive elements:

$$k_o(1-\theta)\exp\left(\frac{n_1 F\varphi_0}{RT}\right) > 0,$$

in case of strong effects of the process of overoxidation on DEL, leading to the autocatalytic filling of the electrode surface with the overoxidated polypyrrole. This can happen if the polypyrrole derivative is a strong reducing agent and thus can form fluctuations

$$k_o h \exp\left(\frac{n_1 F\varphi_0}{RT}\right) > 0,$$

because of the possibility of autocatalytic formation of protons in the process of overoxidation of polypyrrole. This factor was considered as a factor self-oscillating behavior of the overoxidative polypyrrole in [33, 35–36], and this system it also presents.

$$-k_c \alpha\theta c \exp\left(\frac{n_2 F\varphi_0}{RT}\right) > 0,$$

n the case of strong influences on the DEC process of oxidation of cobalt salts to hydroxy-hydroxycobalamine, which, incidentally, has already been described in [15, 16, 34].

In this case because of the greater possibility of positive feedback, the probability of self-oscillations in this system will be higher than in case of simple potentiostatic overoxidation of polypyrrole or the anodic oxidation of cobalt salts.

The stability of the stationary state we analyzed according to the criterion of Routh-Hurwitz. To avoid cumbersome expressions, we introduce new parameters so as the determinant of the Jacobian matrix can be written as:

$$\frac{4}{\delta^2\Gamma}\begin{vmatrix} -\kappa_1 + X & \Sigma & 0 \\ X & \Sigma - \Sigma_3 & -\Lambda \\ 0 & -\Sigma_3 & -\Lambda - \kappa_2 \end{vmatrix}. \quad (17)$$

Using the condition Det $J < 0$, which can be derived from the criterion of Routh-Hurwitz, we obtain the condition of stability of stationary state in the form of inequalities that can be resolved relative to the diffusion coefficient of cobalt salt κ_2:

$$-\kappa_2 < \frac{\Lambda\Sigma_3(\kappa_1 - X)}{\Sigma_3\kappa_1 - \Sigma\kappa_1 - X\Sigma_3}. \quad (18)$$

Or:

$$\kappa_2 > \frac{\Lambda\Sigma_3(X - \kappa_1)}{\Sigma_3\kappa_1 - \Sigma\kappa_1 - X\Sigma_3} - \Lambda. \quad (18)$$

Thus, the stability of the stationary state, in this case, is supported by the more rapid diffusion of cobalt salts than protons and by high oxidation rate, which shifts the right part of inequality towards more negative values (in this case, the left part of the inequality is positive). So, at high concentrations of cobalt salts, the pH-dependence of stability of the stationary state decreases drastically. Thus, for an optimal synthesis of the composite, it is necessary to use a concentration of cobalt salts with a small margin relative to the concentration of pyrrole and pH, but the composite will contain a quite significant proportion of the oxy-hydroxy cobalt compound.

The pH-decreasing leads to an increase in the value of the fraction in the right part of the inequality and, at relatively low concentrations of cobalt salts, also reduces the stabilization trend of a stationary state, even including the system leave from the stationary state, which is displayed at the point of *a monotonic instability*, occurring in the condition of:

$$\kappa_2 > \frac{\Lambda\Sigma_3(X-\kappa_1)}{\Sigma_3\kappa_1 - \Sigma\kappa_1 - X\Sigma_3} - \Lambda\,, \quad (19)$$

represented by a N-shaped part of the voltamperogram. In a common system with potentiostatic overoxidation of polypyrrole, contrarily to this system, it is impossible.

DEL factors also strongly affect the stability of the stationary state in this system. For example, in case of strong effects of electrochemical oxidation of cobalt salts on the structure of the DEC, the parameter Λ will have negative values which will lead to the exit of the stationary state of the field of stability. This factor is also present in other similar systems.

The presence of fluoride ions. As known, oxy-hydroxycompound of cobalt is unstable in the presence of fluoride ions, and dissolves with the formation of the complex $[CoF_6]^{3-}$, according to the total equation:

$$CoO(OH) + 6HF \rightarrow$$
$$\rightarrow H_3[CoF_6] + 2H_2O. \quad (20)$$

In this case, the model isn´t capable to describe the behavior of the composite yet. The stability of the composite in the presence of fluoride ions will be analyzed in one of our next works.

Conclusions

1. The steady-state stability for this system is maintained by relatively high pH and a high concentration of cobalt ions in the surface layer and common to all such systems the absence of strong effects of electrochemical processes on DEL.

2. The oscillatory behavior of this system is possible, being caused not only by the autocatalytic protons´ formation, as for the general case of overoxidation of the conducting polymers, but the influence on the electrochemical reactions of DEC – overoxidation and oxidation of cobalt salts.

A monotonic instability for this system is realized at relatively low pH and the strong effects of electrochemical reactions on the DEC.

1. Sadki S. Scottland Ph., Brodie N., Saboraud G. The mechanisms of pyrrole electropolymerizaion. *Chem. Soc. Rev.* 2000;29(5):283–289.
2. J. Roncali. Conjugated poly(thiophenes): Synthesis, functionalization and applications. *Chem. Rev*. 1992;92(4):711–738.
3. Bodnaryuk-Lupshak N., Aksimentyeva O. I. *Vopr. Khim. Khim. Techn.* 1998; 50:1.
4. Yamamoto T. Molecular assembly and properties of polythiophenes. *NPG Asia Materials.* 2010;2(2):54–60. doi: 10.1038/asiamat.2010.37.
5. Ojani R., Raoof J. B., Ahmady A., Hosseini S. R. *Casp. J. Chem*. 2013;2:45.
6. de Andrade V. M. Confecção de biossensores através da imobilização de biocomponentes por eletropolimerização de pirrol. Tés. M. Eng. UFRGS., Porto Alegre, 2006.
7. Tosar Rovira J. P. Estudio de la inmovilización de oligonucleótidos a eléctrodos

modificados de oro:polipirrol, y detección electroquímica de secuencias complementarias. Tes. Lic. Bioquím., Universidad de la República, Montevideo, 2008.
8. Ramanavicius A., Ramanaviciene A., Malinauskas A. Electrochemical sensors based on conducting polymer-polypyrrole. *Electrochim. Acta*. 2006;51(27):6025–6037. doi: 10.1016/j.electacta. 2005.11.052.
9. Singh R. P. Prospects of Organic Conducting Polymer Modified Electrodes: Enzymosensors. *Int. J. Electrochem*. 2012;502707. URL: http://dx.doi.org/10.1155/2012/502707.
10. Zane D., Appetecchi G. B., Bianchini C., Passerini S., Curulli A. An impedimetric glucose biosensor based on overoxidized polypyrrole thin film. *Electroanalitica*. 2011;23(50):1134–1141. doi: 10.1002/elen.201000576.
11. McQuade T., Pullen A., Swager T. M. Conjugated polymer based chemical sensors. *Chem. Rev*. 2000;100(7):2537–2574. doi: 10.1021/cr9801014.
12. Ojani R., Raoof J. B., Rahemi V. A simple and efficient electrochemical sensor for electrocatalytic reduction of nitrite based on poly94-aminoacetanilide) film using carbon paste electrode. *J. Chin. Chem. Soc*. 2011;58(2):247–254.
13. Sargentelli V., Ferreira A. P. Magnetic nanoparticles: The cobalt. *Ecletica Química*. 2010;35(4):153–163. doi: 10.1590/S0100-46702010000400020.
14. Jamison T. F., Shambayati S., Crowe W. E., Schreiber S. L. Tandem use of cobalt-mediated reactions to synthesize (+)-epoxydictymene, a diterpene containing a trans-fused 5-5ring system. *J. Am. Chem. Soc*. 1997;119(19):4353–4363. doi: 10.1021/ja970022u.
15. Stadnik O. Diss. Kand. Chim. N. Kiev, 2011.
16. O. Stadnik et. al. Int. Electrochem. Soc. Meeting. Abstract # 2240. – 2010.
17. Ansari R. Polypyrrole Conducting Electroactive Polymers: Synthesis and Stability Studies. *E- J. Chem*. 2006;3(4):186–206. LINK: http://downloads.hindawi.com/journals/chem/2006/860413.pdf
18. Ba-Shammakh M. S., Rahman S. U., Abul-Hamayel M. A., Kahraman R. Thermal effects on the process of electropolymerization of pyrrole on mild steel. 203rd ECS Meeting, April 27-May 2, 2003, Paris, France. AC1. Organic and Bioorganic Electrochemistry General Session. No. 2468. LINK: http://www.electrochem.org/dl/ma/203/pdfs/2468.pdf
19. Liu A. S., Oliveira M. A. S. Electrodeposition of polypyrrole films on aluminum from tartrate aqueous solution. *J. Braz. Chem.Soc*. 2007;18(1):143–152.
20. Sazou D. The dynamical behavior of the electrochemical polymerization of indole on Fe in acetonitrile-water mixtures. *Synthetic Metals*. 2002;130(1):45–54. doi: 10.1016/S0379-6779(02)00110-8.
21. Das I., Goel N., Agrawal N. R., Gupta S. K. Growth patterns of dendrimers and electric potential oscillations during electropolymerization of pyrrole using mono- and mixed surfactants. *J. Phys. Chem*.-B. 2010;114(40):12888–12896. doi: 10.1021/jp105183q.
22. Bazzaoui M., Bazzaoui E. A., Martins L., Martins J. I. Electropolymerization of pyrrole on zinc-lead-silver alloys electrodes in acidic and neutral organic media.

Synthetic Metals. 2002;130(1):73–83. doi: 10.1016/S0379-6779(02)00101-7.
23. Das I., Goel N., Gupta S. K., Agrawal N. R. Electropolymerization of pyrrole: Dendrimers, nano-sized patterns and oscillations in potential in presence of aromatic and aliphatic surfactants. *J. Electroanal. Chem*. 2012;670(1):1–10. doi: 10.1016/j.jelechem.2012.01.023.
24. Aoki K., Mukoyama I., Chen J. Competition between polymerization and dissolution of poly(3-methylthiophene) films. *Russ. J. Electrochem.* 2004;40(3):280–285. doi: 10.1023/B:RUEL.0000019665.59805.4c.
25. Das I., Agrawal N. R., Ansari S. A., Gupta S. K. Pattern formation and oscillatory electropolymerization of thiophene. *Ind. J. Chem.-A*. 2008;47(12):1798–1803.
26. Ba-Shammakh M. S. Electropolymerization of pyrrole on mild steel for corrosion protection. Thes. Ph. D. King Fahd University of Petroleum and Minerals Dharan, Saudi Arabia, 2002.
27. Pagitsas M., Dimitra S. The improved Franck-FitzHung model for the electrodissolution of iron in sulphuric acid solutions: linear stability and bifurcation analysis. Derivation of the kinetic equations for the forced franck-FitzHung models. *Electrochimica Acta*. 1991;36(8):1301–1308. doi: 10.1016/0013-4686(91)80009-w.
28. Pearlstein A. J., Johnson J. A. Global and conditional stability of the steady and periodic solutions of the Franck-FitzHugh model of electrodissolution of Fe in H_2SO_4. *J. Electrochem. Soc.* 1989;136(5):1290–1299.
29. Ogüz Güler M.et. al. 7th Turkish Nanoscience and Nanotechnology Conference. 2011. P. 24.
30. Roncali J. Conjugated poly(thiophenes): Synthesis, functionalization and applications. *Chem. Rev*. 1992;92(4):711–738.
31. Lemos Castagno K. R. Tés. D. Sc. UFRS., Porto Alegre, 2006.
32. Mostany J., Scharifker B. R. Impedance spectroscopy of undoped, doped and overoxidazrd polypyrrole films. *Synthetic Metals*. 1997;87(3):179–185.
33. Tkach V., Nechyporuk V., Yagodynets´ P., Rusnak I. *Orbital. Elec. J. Chem*. 2012;4:136.
34. Tkach V., Nechyporuk V., Slipenyuk O. *Ecl. Quím*. 2012;37:72.
35. Ткач В. В., да Роша Ал. М. *Наук. Вісник ЧНУ*. 2013;658:132.
36. Tkach V., Nechyporuk V., Yagodynets P. Electropolymerization of heterocyclic compounds. Mathematical models. *Ciencia e Tecnnjlogia dos Materials*. 2012;24(1–2):54–58.
37. Tkach V., Nechyporuk V., Yagodynets´ P. *Proc. Quím*. 2014;8:49.
38. Tkach V., Nechyporuk V., Yagodynets´ P. Hryhoryak M. *Cien. Techn. Mat*. 2012;24:50.
39. Tkach V., Nechyporuk V., Yagodynets´ P. *Tecn. Met. Mat. Min.* 2013;10:249.
40. Tkach V., Nechyporuk V., Yagodynets P. Description matematica de la sintesis electroquimica de polimeros conductors en la presencia de surfactants. *Avances en Química*. 2013;8(1):9–15.
41. Tkach V., Nechyporuk V., Yagodynets´ P. *Avan. Quím*. 2013;8:97.

42. Tkach V., Nechyporuk V., Yagodynets P. The mathematical stability investigation in the electrochemical polymerization of heterocyclic compounds in the oxidants' presence. *Afinidad*. 2013;70(561):70–74.
43. Tkach V. V., Nechyporuk V. V., Yagodynets P. I. de Oliveira S. C., de Rocha Al. M. The Mathematical Description for the electropolymerization of electrochemical modified monomers in Galvanostatic Mode. *J. of Sib. Fed. Univ. Chemistry.* 2014;7(3):403. URL: http://elib.sfu-kras.ru/handle/2311/13421.
44. Tkach V., Nechyporuk V., Yagodynets´ P. Anais do 10o Encontro Brasileiro sobre Adsorção, Guarujá, SP, 27–30 de abril de 2014. 122(1).
45. Tkach V., Nechyporuk V., Yagodynets´ P. *Med. J. Chem*. 2015;3:1122.
46. Tkach V., Nechyporuk V., Yagodynets P. The mathematical stability study of the work of isomerization sensors, based on conduction polymers. *Anal. Bioanal. Electrochem*. 2014;6(3):273–283.
47. Tkach V., Kumara Swamy B., Ojani R., Blanes M., Yagodynets´ P. *Orbital Elec. J. Chem*. 2015;7:1.
48. Tkach V., Ojani R., Nechyporuk V., Yagodynets P. Rev. *Colomb. Cien. Quím. Farm*. 2014;43:35.
49. Tkach V., Ojani R., Nechyporuk V., Yagodynets´ P. *Orbital. Elec. J. Chem*. 2014;6:142.